

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>P804032/WO/1</b>	<div style="display: flex; justify-content: space-between;"> <span><b>FOR FURTHER ACTION</b></span> <span>See Form PCT/IPEA/416</span> </div>	
International application No. <b>PCT/DE 03/03645</b>	International filing date ( <i>day/month/year</i> ) <b>11/03/2003</b>	Priority date ( <i>day/month/year</i> ) <b>11/07/2002</b>
International Patent Classification (IPC) or national classification and IPC  <b>C23C18/16</b>		
Applicant <b>MTU AERO ENGINES GMBH et al.</b>		

1.	This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2.	This REPORT consists of a total of _____ sheets, including this cover sheet.
3.	<p>This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> (sent to the applicant and to the International Bureau) a total of <u>9</u> sheets, as follows:</p> <div style="margin-left: 20px;"> <input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).                <input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.           </div> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) _____, containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>
4.	<p>This report contains indications relating to the following items:</p> <div style="margin-left: 20px;"> <input checked="" type="checkbox"/> Box No. I    Basis of the report              <input type="checkbox"/> Box No. II    Priority              <input type="checkbox"/> Box No. III    Non-establishment of opinion with regard to novelty, inventive step and industrial applicability              <input type="checkbox"/> Box No. IV    Lack of unity of invention              <input checked="" type="checkbox"/> Box No. V    Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement              <input type="checkbox"/> Box No. VI    Certain documents cited              <input type="checkbox"/> Box No. VII    Certain defects in the international application              <input type="checkbox"/> Box No. VIII    Certain observations on the international application           </div>

Date of submission of the demand <b>05/14/2004</b>	Date of completion of this report <b>01/17/2005</b>
Name and mailing address of the IPEA/  Facsimile No.	Authorized officer <b>Hintermaier, F.</b>  Telephone No.

# INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/DE 03/03645

## Box No. I Basis of the report

1. With regard to the language, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

- ☐ This report is based on translations from the original language into the following language \_\_\_\_\_, which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
  - ☐ publication of the international application (under Rule 12.4)
  - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the elements of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

- ☐ the international application as originally filed/furnished
- ☒ the description:
- pages 1-11 \_\_\_\_\_ as originally filed/furnished
- pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_
- pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_
- ☒ the claims:
- pages 2-8 \_\_\_\_\_ as originally filed/furnished
- pages\* \_\_\_\_\_ as amended (together with any statement) under Article 19
- pages\* 1 \_\_\_\_\_ received by this Authority on 09/17/2004 w/ letter 09/17/04
- pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_
- ☐ the drawings:
- pages \_\_\_\_\_ as originally filed/furnished
- pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_
- pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_
- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages \_\_\_\_\_
- ☐ the claims, Nos. \_\_\_\_\_
- ☐ the drawings, sheets/figs \_\_\_\_\_
- ☐ the sequence listing (*specify*): \_\_\_\_\_
- ☐ any table(s) related to sequence listing (*specify*): \_\_\_\_\_

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages \_\_\_\_\_
- ☐ the claims, Nos. \_\_\_\_\_
- ☐ the drawings, sheets/figs \_\_\_\_\_
- ☐ the sequence listing (*specify*): \_\_\_\_\_
- ☐ any table(s) related to sequence listing (*specify*): \_\_\_\_\_

\* If item 4 applies, some or all of those sheets may be marked "superseded."

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### 1. Statement

## Claims

1-7

YES

## Claims

8

NO

## Claims

YES

## Claims

1-7

NO

## Claims

1-8

**YES**

## Claims

NO

see appended sheet

Re Point V.

**Substantiated Determination under Rule 66.2(a)(ii), Regarding  
Novelty, Inventive Activity, and Industrial Applicability;  
Documents and Explanations in Support of this Determination**

1. The following documents cited in the search report are  
named in this report of examination:

D1: DE 40 24,911 A (ASEA BROWN BOVERI) April 11, 1991  
(1991-04-11)

D2: US-A-4,895,625 (THOMA[sic] MARTIN ET AL) Jan. 23,  
1990 (1990-01-23)

D3: DE 37 16 935 A (MOTOREN TURBINEN UNION) December 1,  
1988 (1988-12-01)

D4: SU-A-1 803 480 (DNEPROVSKIJ NII T MASH; N PROIZV OB  
EDINENIE MASH (SU) March 23, 1993 (1993-03-23)

D5: EP-A-0 748,394 (SERMATECH INT INC) December 18, 1996  
(1996-12-18)

D6: WO 94/1,9583 A (BAJ COATINGS LTD; FOSTER JOHN (GB);  
TAYLOR ALAN (GB); CHATTERLEY M) September 1, 1994  
(1994-09-01)

D7: US-A-5,935,407 (NENOV KRASSIMIR P ET AL) August 10,  
1999 (1999-08-10)

D8 WO 00/36180 A (JOSSO PIERRE; BACOS MARIE PIERRE  
(FR); ONERA (OFF NAT AEROSPATIALE) June 22, 2000  
(2000-06-22)

2. Background Information.

- 2.1. D1 relates to the galvanic deposit of protective layers to apparatus parts that are exposed to oxidation and corrosion at high temperatures, such as in turbines (column 1, lines 6 - 11). In exemplary embodiment 1, which is greatly analogous to the exemplary embodiment of page 10 of the present Application, a gas turbine blade made of a nickel superalloy is first degreased and then pickled anodically in diluted HCl. Then a 1  $\mu\text{m}$  Ni adhesion promoting layer is applied galvanically. Subsequently, 150 g of a Ni/Al powder, having a grain size of 10 - 50  $\mu\text{m}$ , are suspended in a 2.5 l nickel sulfamate bath. Depositing takes place at a current density of 500A/m<sup>2</sup>. The bath is vibrated for this. The additionally added glass balls support the suspension and also make denser the galvanically deposited layer. A layer having a thickness of 1 mm is produced, which is subsequently exposed to homogenization at 1100°C for 3 hours.
- 2.2. D2 describes the production of protective coatings on component parts that are in contact with corrosive hot gas, such as gas turbine parts (column 1, lines 7 - 9). According to Claim 1, an electrolyte based on Co and or nickel is made available for this, in which a passivated powder of a metal alloy of Al and/or Cr is suspended. In this instance, the powder does not necessarily have to contain Cr. By passivating is meant providing the particles with an artificial oxide layer. After the galvanic deposit, the substrate is tempered. The powder has a particle size of 1 - 15  $\mu\text{m}$ .

- 2.3. D3 describes the preparation of a hot gas corrosion protective layer, e.g. on turbine blades. For this, in a  $\text{NiSO}_4$  or in a  $\text{CoSO}_4$  electrolytic bath,  $\text{TiSi}_2$  particles having a diameter of 0.5 - 50  $\mu\text{m}$  are suspended and a 10 - 1000  $\mu\text{m}$  thick layer is deposited galvanically. In closing, tempering is carried out at 800°C (column 2, lines 21 - 56).
- 2.4. D4 also states a process for improving the corrosion resistance of component parts that are exposed to hot gas. For this purpose, a mixture of Al and W particles is suspended in a Ni electrolyte, and a protective layer is deposited which is tempered at 1200°C. Before being applied, the aluminum particles are treated with  $\text{H}_2\text{SO}_4$ , then washed and tempered in air at 190 - 230°C. In this context, an artificial oxide layer is generated on the Al particles.
- 2.5. D5, which is cited in the present Application, describes the improvement of the corrosion properties and the oxidation properties of turbine parts by applying a protective layer made of Al particles and Si particles, and is subsequently diffused in by heat treatment [0001, 0002, 0039 - 0049]. In [0012] and [0013] a protective layer from the related art is cited which is also made of Al particles and Si particles.
- 2.6. Finally, it is noted that it is part of the related art to improve the corrosion properties of parts exposed to hot gases, using protective coatings, which were obtained by galvanic depositing of particles based on Cr-Al-Y and

subsequent tempering (D6, D7). Currentless methods for depositing such layers are also known (D8).

3. Novelty (Article 33(2)PCT)

3.1. Claim 1 appears to be novel, since none of documents D1 - D8 describes an external currentless or electrolytic depositing of Pt to which additional particles have been added.

3.2. Claim 8 does not appear to be novel, since it is not clear why a protective layer produced by the method according to Claim 1 would be different from a layer produced according to the method as in D5. In D5 a layer is deposited successively that includes metals, which are also mentioned in Claim 1 of the present Application. This layer is tempered, same as that of Claim 1, the final protective layer being created thereby.

4. Inventive Step (Article 33(3) PCT).

4.1. D1 - D4 state methods that include all the technical elements of Claim 1 except that in D1 - D4 Ni and/or Co is deposited instead of Pt in an external currentless or electrolytic manner. D6 - D8 also state methods in which particles are applied to a substrate together with a metal, by external currentless or electrolytic deposition of this metal. In all the cases D1 - D4 and D6 - D8 articles are coated, in this context, that are exposed to hot gas corrosion. By subsequent tempering of

the deposited layer, an alloy formation is achieved in this context, and the protective layer is formed.

- 4.2. It is sufficiently well known that the protective layers of such articles may also contain Pt. Thus, for example, D5 states that one should first deposit Pt **electrolytically** on the surface of a respective component, then apply a slurry of aluminum and silicon powder, and subsequently sinter at 660°C [0046, 0040]. D8 also mentions using noble metals in such coatings, Pt and Pd being preferred (Claims 1 and 4).
- 4.3. Consequently, it appears obvious also to use Pt-containing electrolytes in conjunction with the methods named in D1 - D4 and D6 - D8 in producing hot gas corrosion protective layers, in order to arrive at a matrix of Pt-containing metal and particles which form said protective layer after a tempering step. In addition, D5 already makes it obvious that one should consider depositing Pt electrolytically for building up such corrosion protective layers. And finally, the present Application states no surprising effects that would be attributable to the use of Pt instead of Ni or Co in the electrolyte.
- 4.4. The further technical elements of dependent Claims 2 - 8 are already mentioned in documents D1 - D8, or may be found by customary experimental activity. Thus, D1 already mentions the use of particles alloyed with Ni, having a grain size of 10 - 50 µm. In D2 a passivated powder is used which actually includes particles having

an artificial oxide layer. In D3,  $\text{TiSi}_2$  particles are used as the powder. The use of Si particles for improving the corrosion properties is known from D5. The ascertainment of the optimal thickness of the protective layer is regarded as a routine method.

4.5. Finally, it is noted that it is part of the related art to improve the corrosion properties of parts exposed to hot gases, using protective coatings, which were obtained by galvanic depositing of particles based on Cr-Al-Y and subsequent tempering (D6, D7). Currentless methods for depositing such layers are also known (D8). The exclusion of Cr as component of the particles in Claim 1 consequently appears to be only the desire to produce novelty as compared to methods known per se. In any case, special non-obvious technical effects are not described for the exclusion of Cr in the present Application. On the contrary: according to page 3, lines 15 - 16, Cr may even be present.

#### 5. Industrial Applicability.

Claims 1 - 8 satisfy the requirement of industrial applicability (Article 33(4) PCT), since the technical subject matter of the present Application may be industrially manufactured or used in a technical sense.

Re Point VII

**Certain Defects in the International Application**

The present Application does not correspond to the requirements of Rule 5.1(a)(ii)PCT, since the most proximate related art, e.g. documents D1 - D3 are neither mentioned in the introduction to the present invention nor is their content cited briefly.

Re Section VIII

**Specific Remarks regarding the International Application 1.**

1. Clarity

1.1. Claim 1 contradicts the specification on page 3, lines 15 - 16, according to which the particles do not contain any Cr preferably, but not necessarily.

1.2. The definition of the oxide layer in Claim 2 is formulated in a vague manner: what are „normal environmental conditions“? This objection could be removed by making the thickness of the oxide layer more precise according to what is said on page 7, lines 23 - 25.

1.3. Having Claim 5 dependent on Claim 4 makes little sense: Si particles that are alloyed with Si.

2. The present Application does not satisfy the requirements of Article 5, PCT, since it does not put one skilled in the art into the position of executing the subject matter of Claim 1. Thus, the Application states no exemplary

embodiment from which it would be clear how the  
depositing using a Pt electrolyte would proceed, and  
which electrolyte would be appropriate for this.

## New Claim

What Is Claimed Is:

1. A method for coating a substrate, having the following steps
  - a) external current-less or electrolytic deposition of Pt or Pt and Co in a deposition bath known as such, in which additionally particles are suspended which contain at least one metal selected from Mg, Al, Ti, Zn and no Cr, the particles becoming occluded in the coating
  - b) heat treatment of the coated substrate.